Supporting Information

Cobalt(II) Complexes with *N,N,N*-Scorpionates and Bidentate Ligands: Comparison of Hydrotris(3,5-dimethylpyrazol-1-yl)borate Tp* vs. Phenyltris(4,4-dimethyloxazolin-2-yl)borate To^{M} to Control the Structural Properties and Reactivities of Cobalt Centers

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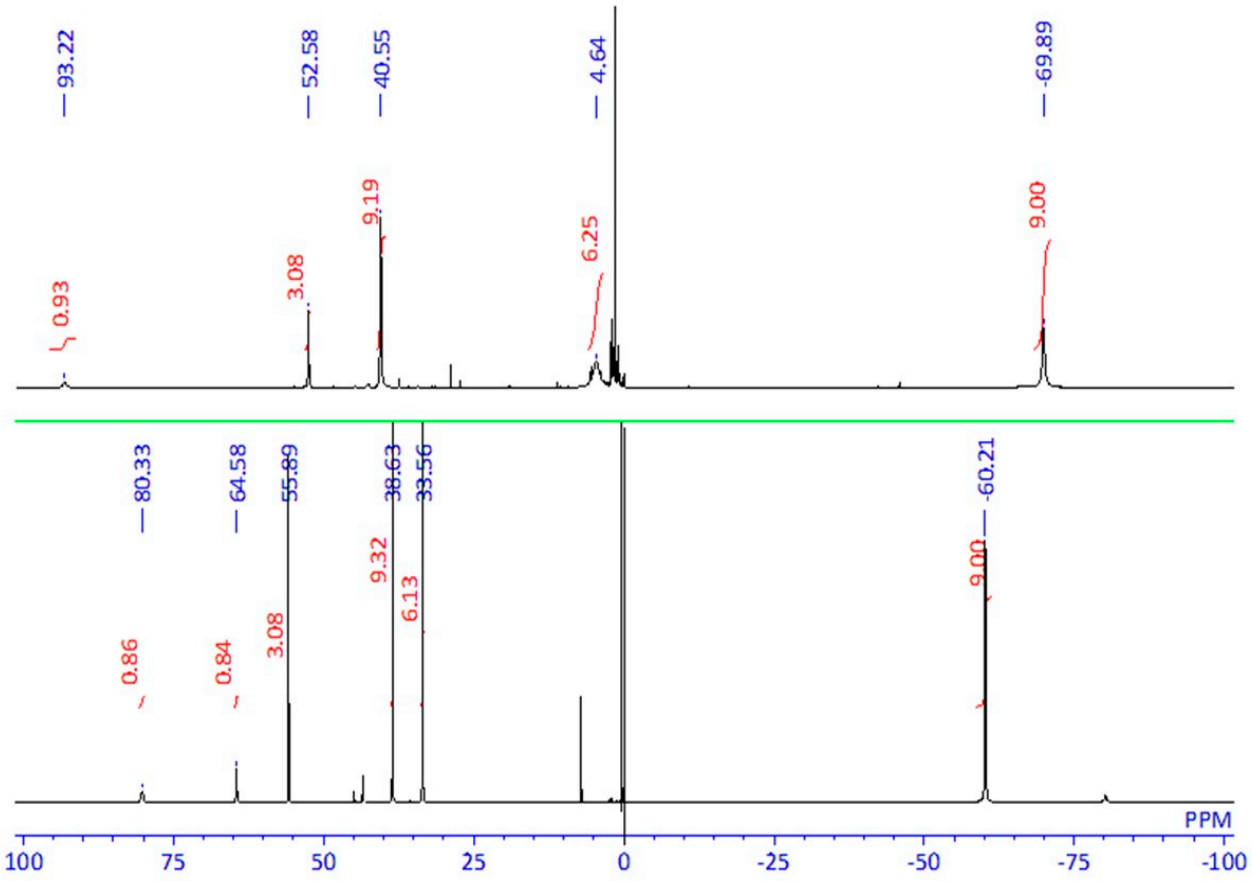

Figure S1. ^{1}H-NMR spectra of the CD_3CN (**top**) and $CDCl_3$ (**bottom**) solutions of [Co^{II}(acac)(Tp*)] (**1**) (600 MHz; measured at ambient temperature).

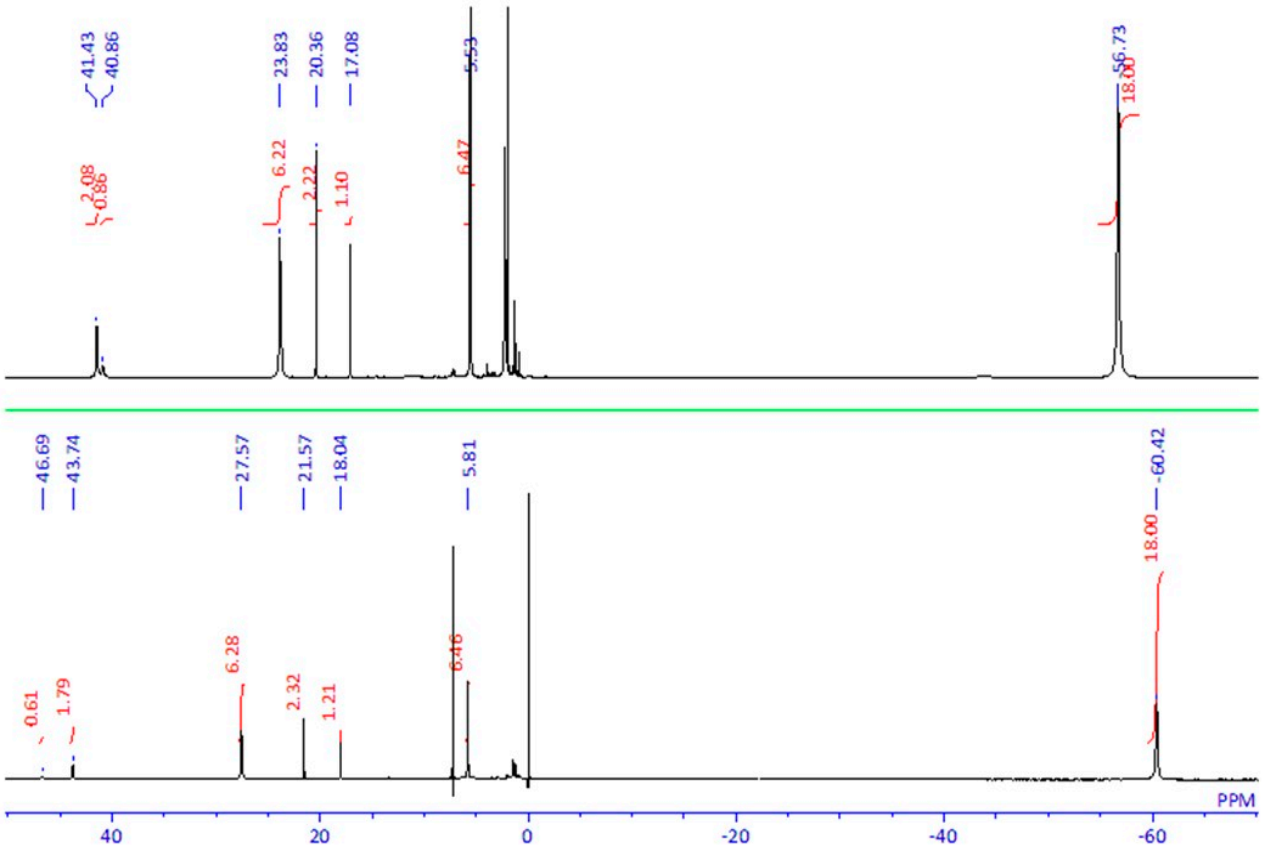

Figure S2. ^{1}H-NMR spectra of the CD_3CN (**top**) and $CDCl_3$ (**bottom**) solutions of [Co^{II}(acac)(To^{M})] (**2**) (600 MHz; measured at ambient temperature).

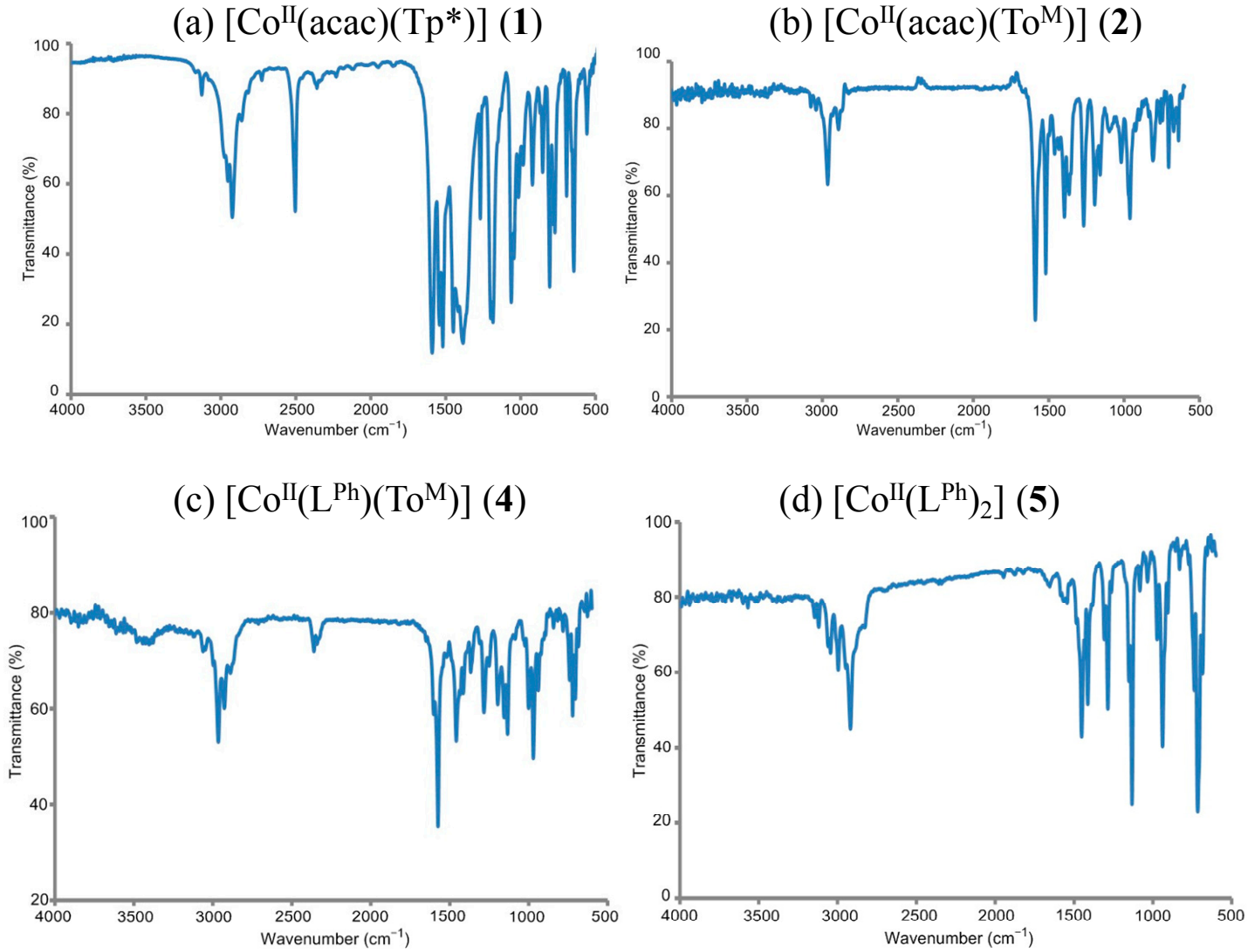

Figure S3. FT/IR spectra of KBr pellets of [Co^{II}(acac)(Tp*)] (**1**; (**a**)), [Co^{II}(acac)(To^{M})] (**2**; (**b**)), [Co^{II}(L^{Ph})(To^{M})] (**4**; (**c**)) and [Co^{II}(L^{Ph})$_2$] (**5**; (**d**)) measured at room temperature.

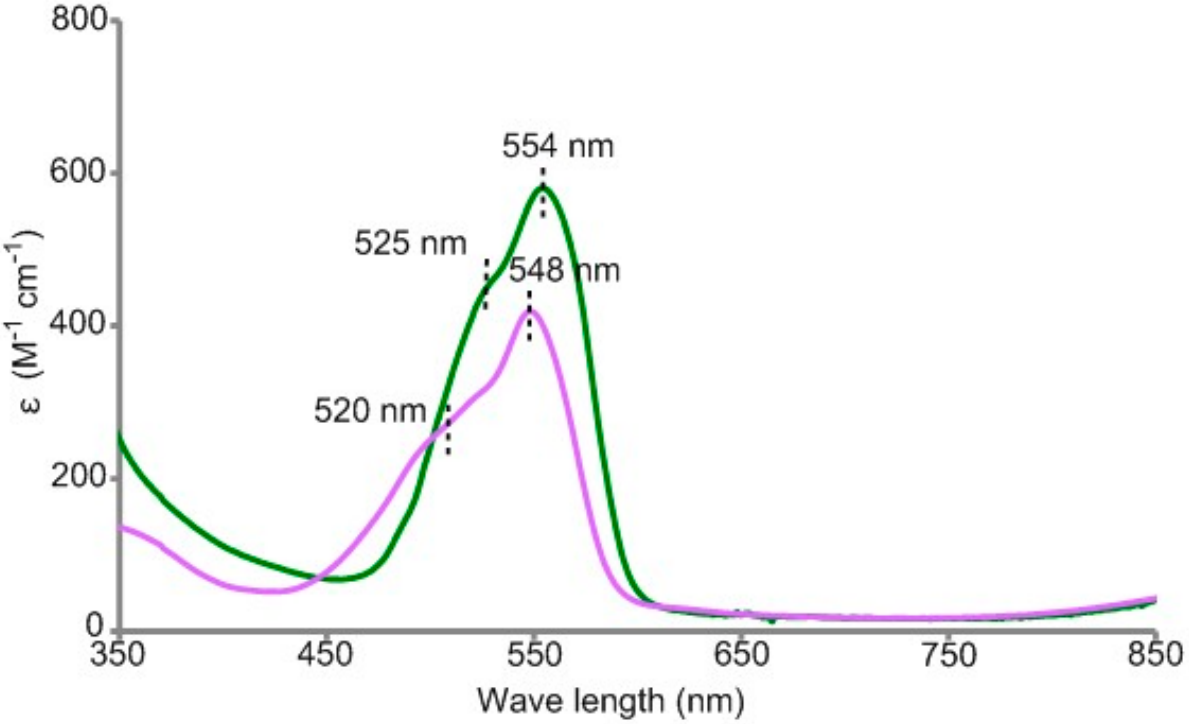

Figure S4. UV-vis spectra of the CH_2Cl_2 solutions of $[Co^{II}(To^{M})(L^{Ph})_2]$ (**4** ; green) and$[Co^{II}(L^{Ph})_2]$ (**5** ; purple) measured at room temperature.

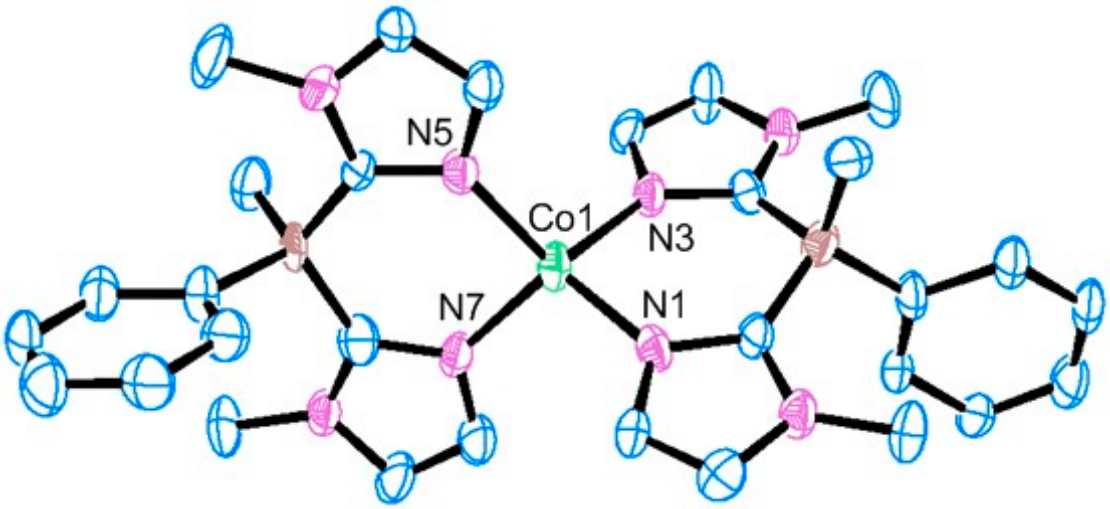

Figure S5. Molecular structure of **5**. All hydrogen atoms are omitted for clarity; thermal ellipsoids are set at 30% probability. Selected bond lengths [Å] and angles [°]: Co1-N1 1.997 (8), Co1-N3 1.992 (8), Co1-N5 1.996 (8), Co1-N7 1.994 (8), N1-Co1-N3 95.8 (3), N1-Co1-N5 125.5 (3), N1-Co1-N7 108.2 (3), N3-Co1-N5 109.3 (3), N3-Co1-N7 123.7 (3), N5-Co1-N7 96.9 (3).

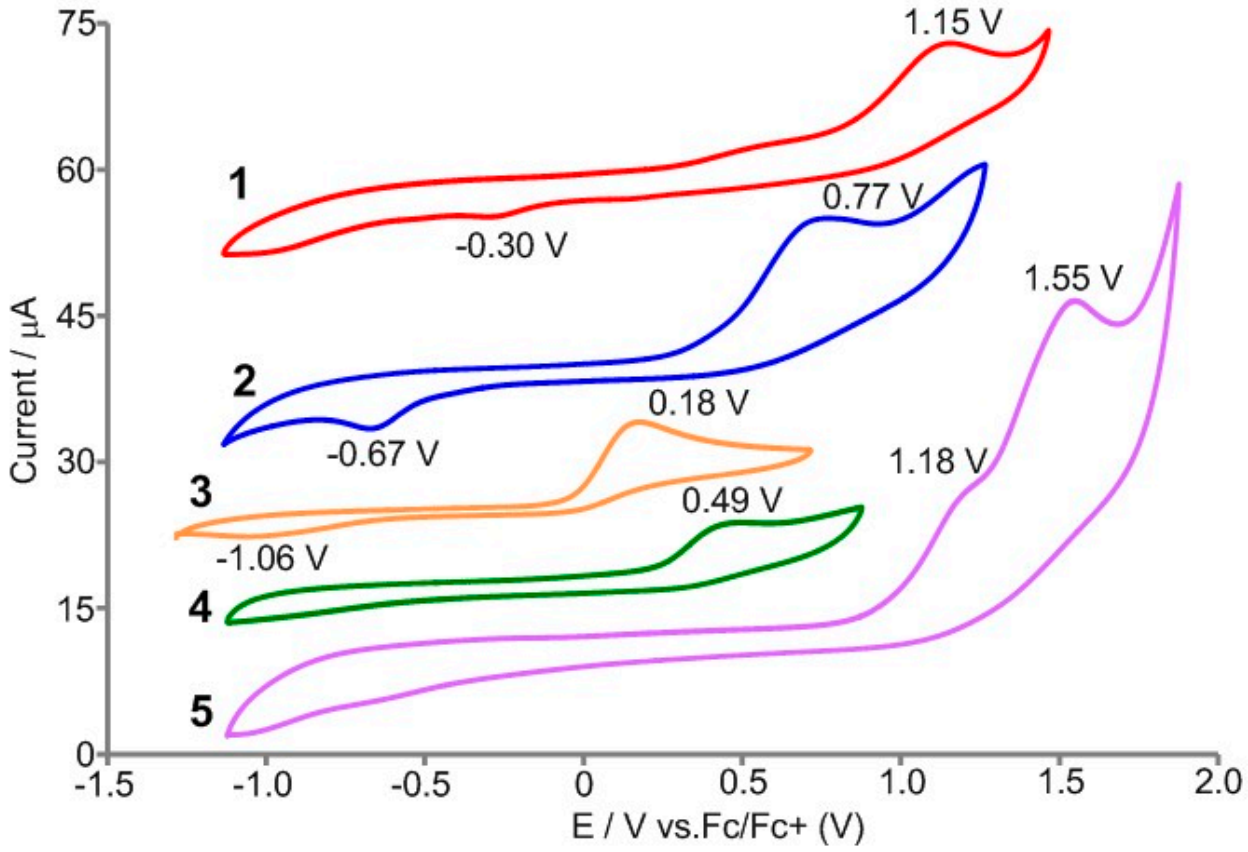

Figure S6. Cyclic voltammograms of **1**–**5**. Measurement conditions: working electrode; Pt disc, counter electrode; Pt wire, reference electrode; Ag/AgCl, amount of cobalt(II) complexes; 5 μmol, solvent; MeCN (for **1**, **2**, **4**, **5**) and CH_2Cl_2 (for **3**), supporting electrolyte; $(^nBu_4N)PF_6$ 0.1 M, atmosphere; Ar, temperature; ambient temp. scan rate : 100 mV/s.

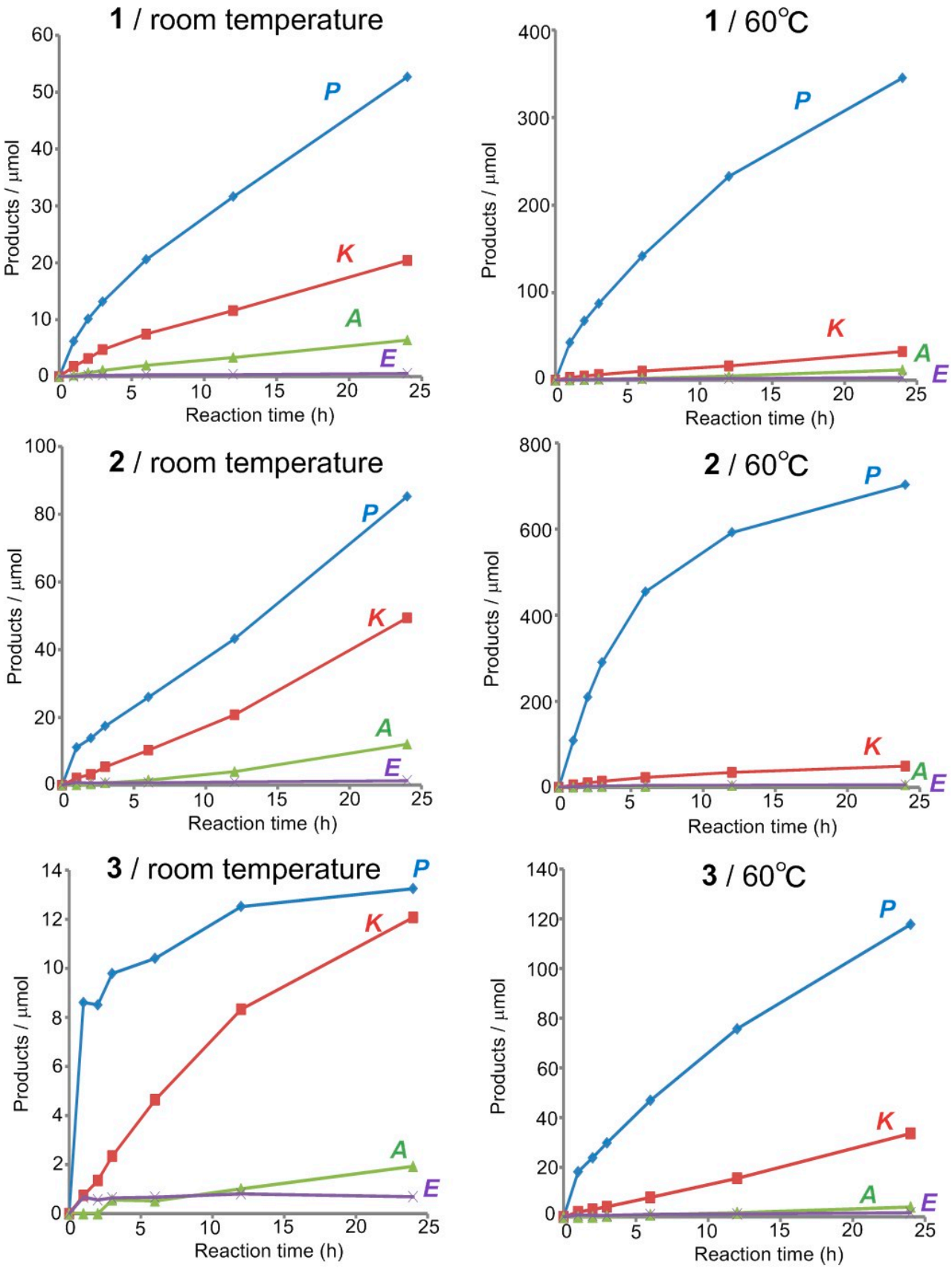

Figure S7. Time course of cyclohexene oxidation with TBHP mediated by **1–6**, $Co^{II}(acac)_2 \cdot 2H_2O$ and $Co^{II}(OAc)_2 \cdot 4H_2O$.

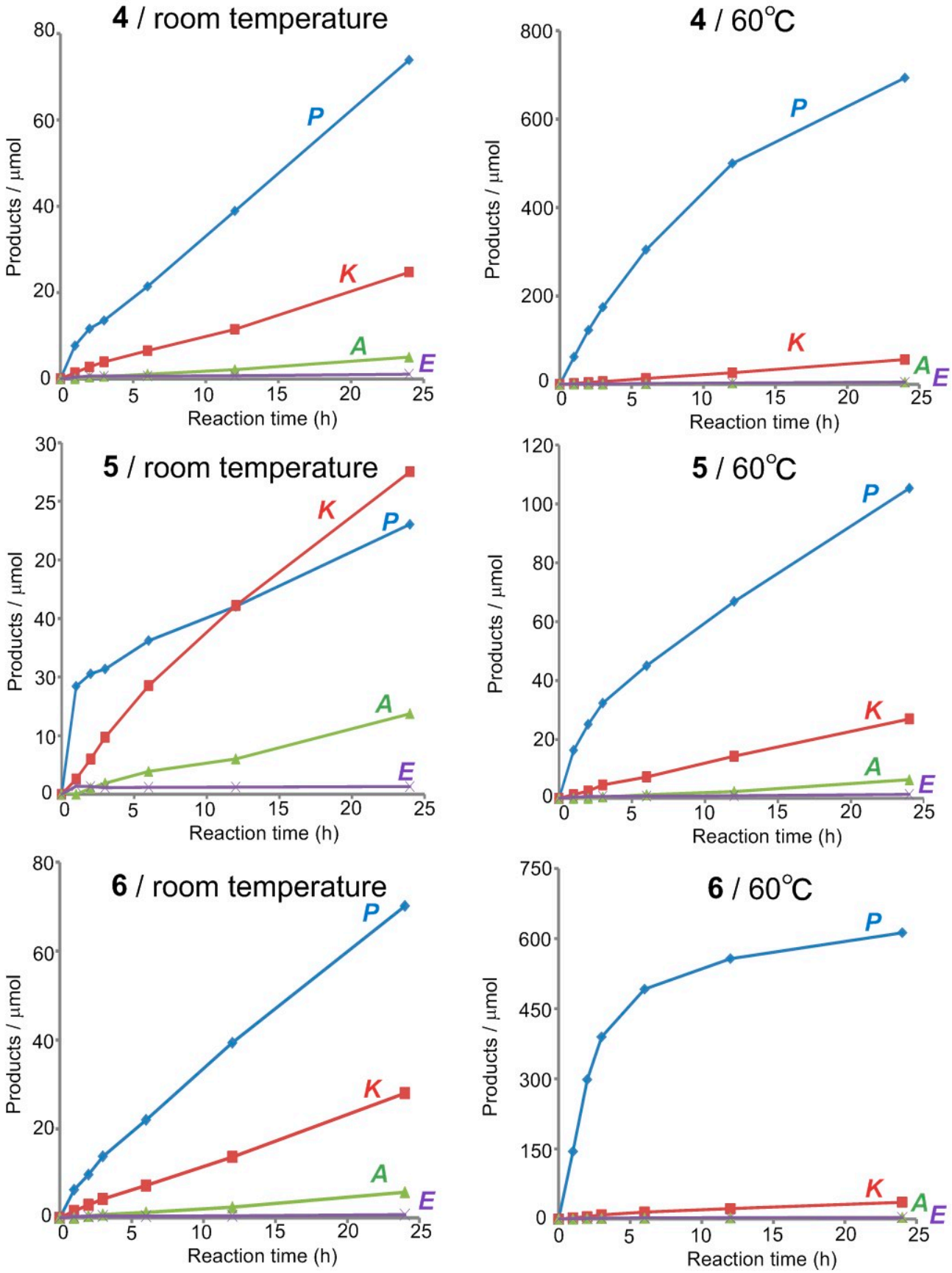

Figure S7. (continued)

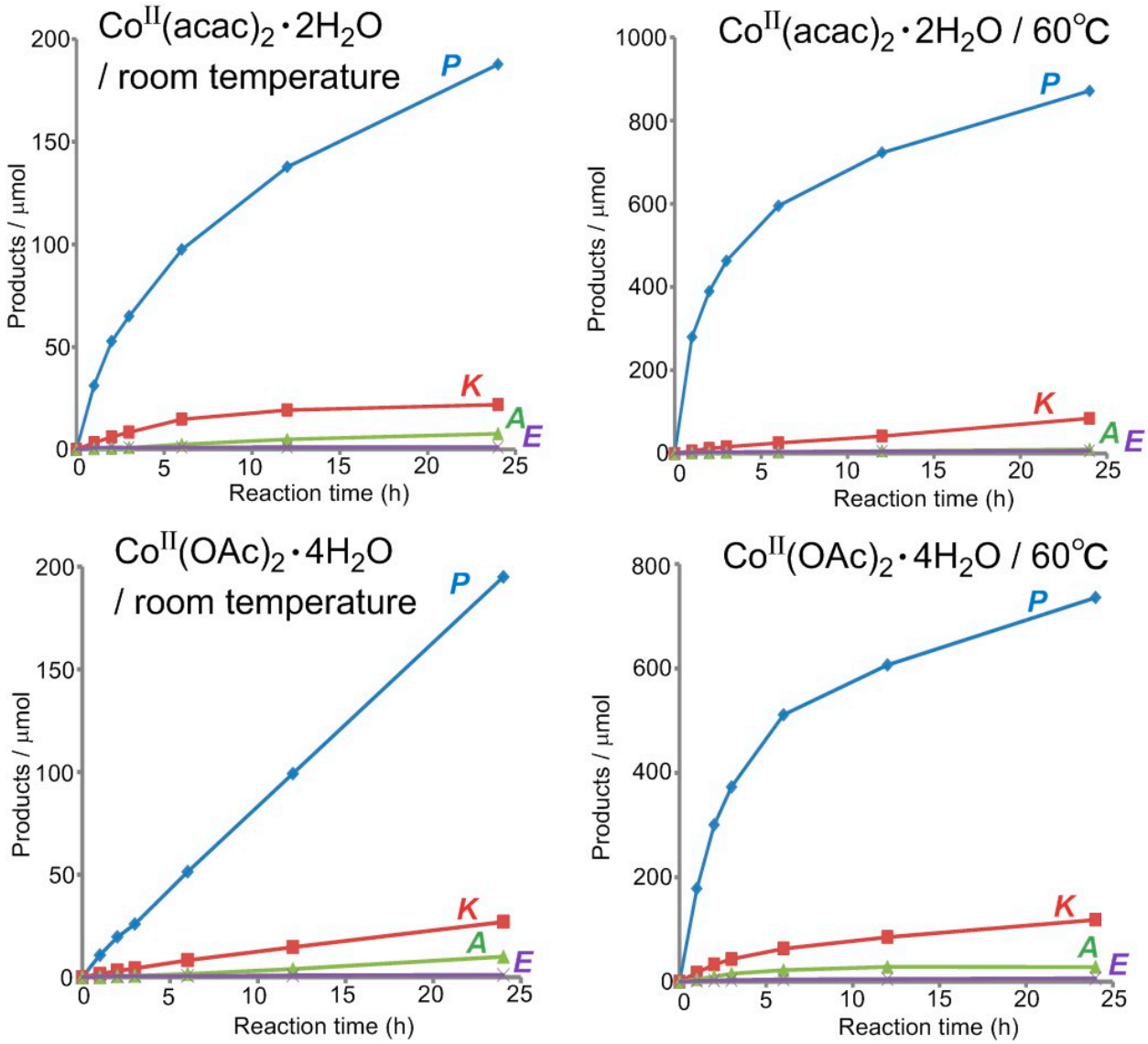

Figure **S7.** (continued)

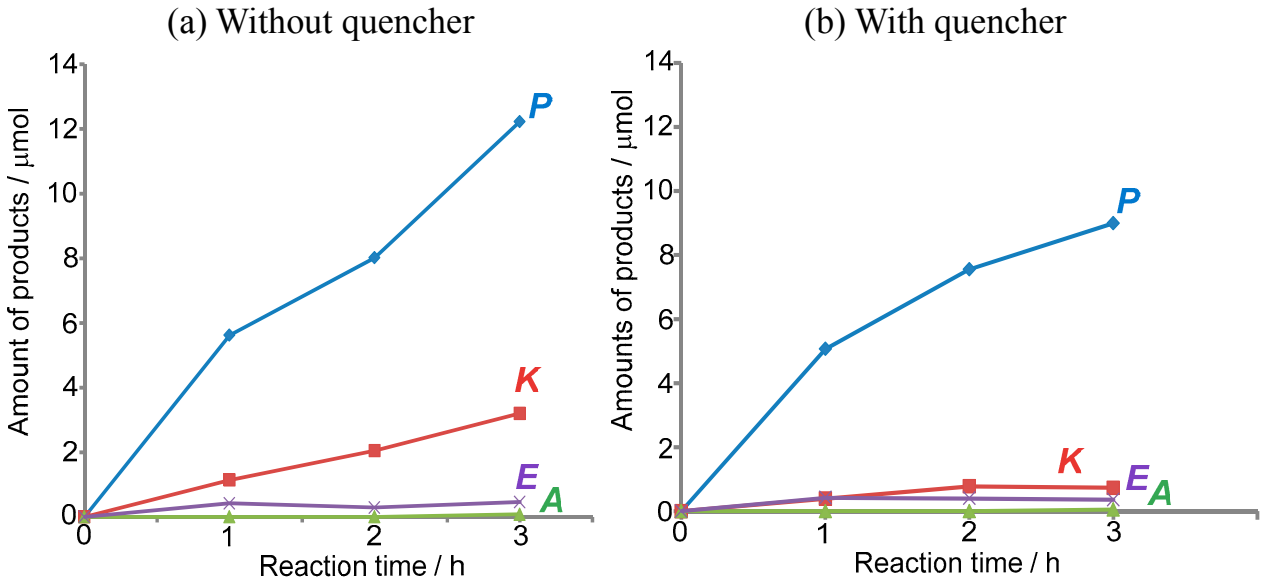

Figure S8. Products analysis for the cyclohexene oxidation with TBHP by **2** at ambient temperature with or without of the PPh_3 quencher.

Table S1. Crystallographic data and structure refinement parameters for **1**, **2**, **4** and **5**.

Complex	**1**·MeCN	**2**·(pentane)$_{0.5}$	**4**	**5**
Formula	$C_{22}H_{32}BCoN_7O_2$	$C_{26}H_{36}BCoN_3O_5\cdot(C_5H_{12})_{0.5}$	$C_{36}H_{47}B_2CoN_7O_3$	$C_{30}H_{36}B_2CoN_8$
Formula weight	496.28	576.41	706.35	589.22
Crystal color, habit	Pink, Block	Purple, Block	Purple, Block	Red, Block
Size/mm	0.20, 0.30, 0.40	0.20, 0.20, 0.50	0.05, 0.15, 0.25	0.05, 0.25, 0.35
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$ (#14)	$P2_1/n$ (#14)	P-1 (#2)	$P2_1/n$ (#14)
a/Å	11.2775(6)	9.006(3)	11.039(8)	19.87(2)
b/Å	19.0252(9)	22.243(7)	11.658(8)	7.585(9)
c/Å	12.1374(9)	15.742(5)	14.845(11)	21.65(3)
α/deg	90	90	80.14(2)	90
β/deg	100.542(3)	105.644(4)	89.58(2)	100.02(2)
γ/deg	90	90	88.50(3)	90
V/Å^3	2260.2(2)	3036.6(4)	1881.5(7)	3213(7)
Z	4	4	2	4
F(000)	1044	1224	746	1236
D(calcd)/g·cm^{-3}	1.288	1.261	1.247	1.218
μ (Mo-Kα) cm^{-1}	7.02	6.05	5.00	5.66
Temp./K	113	133	113	113
Unique reflections	5843	6694	7821	6469
Observed reflections $I > 2\sigma(I)$	5291	5746	4858	1160
Parameter refined	311	438	452	376
$2\theta_{max}$/deg	55.0	55.0	54.6	54.0
$R(I > 2\sigma(I)$, all)[a]	0.0338, 0.0388	0.0314, 0.0374	0.0682, 0.1051	0.120, 0.247
$R_w(I > 2\sigma(I)$, all)[a]	0.0815, 0.0846	0.0815, 0.0849	0.1684, 0.1992	0.270, 0.365
Goodness of fit S[b]	1.061	1.045	1.022	0.784

[a] $R = \sum||F_o| - |F_c|| / \sum|Fo|$. $R_w = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$. [b] $S = \{\sum[w(F_o^2 - Fc^2)^2] / (n\text{-}p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.